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14. ABSTRACT
Our LOCO research program explores two closely related projects that seek to employ resonant plasmonic phenomenon for the generation of low-temperature, electrochemical and photochemical potentials within the optical near-field of nanoscale plasmonic structures. We have worked to develop a plasmon-driven source for controlled deposition of nitrogen precursors for low temperature nitride film growth using cryogenically cooled, plasmonically active patterned substracts. Separately, we have also performed theoretical and experimental identification of a newly described optoelectronic phenomenon, termed the "plasmoelectric effect", whereby

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Harry Atwater
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Report Title

Final Report: Low Temperature Locally-Controlled Plasmon Resonance-Excited Kinetic Processes

ABSTRACT

Our LOCO research program explores two closely related projects that seek to employ resonant plasmonic phenomenon for the generation of low-temperature, electrochemical and photochemical potentials within the optical near-field of nanoscale plasmonic structures. We have worked to develop a plasmon-driven source for controlled deposition of nitrogen precursors for low temperature nitride film growth using cryogenically cooled, plasmonically active patterned substracts. Separately, we have also performed theoretical and experimental identification of a newly described optoelectronic phenomenon, termed the "plasmoelectric effect", whereby plasmonic excitation of metal nanostructures can directly induce electrochemical potentials for electro-reduction and other forms of electrical work.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

9/12/13 Annual Meeting of the America Chemical Society (FALL ACS) "Plasmoelectric Potentials In Metal Nanostructures" Indianapolis, IN

8/20/13 SPIE Optic and Photonic Annual Meeting "Plasoelectric Potentials in Au Colloidal Nanoparticle Assemblies", San Diego CA

Number of Presentations: 2.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Siying Peng	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Matthew Sheldon	0.70
FTE Equivalent:	**0.70**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Harry Atwater	0.03	No
William Goddard	0.02	Yes
FTE Equivalent:	**0.05**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Please see attachment

Technology Transfer

Technical Report to the
Defense Advanced Research Agency
DARPA Grant NO. W911NF-13-1-0040

Attention:
Drs. Tyler McQuade and Anne Fischer
Defense Sciences Office
Defense Advanced Research Projects Agency

"Low Temperature Locally-Controlled Growth of Wide Bandgap Nitride and Diamond Films via Plasmon Resonance-Excited Kinetic Processes"

California Institute of Technology

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Date: 6/18/2015

1. Summary of results for low temperature surface plasmon mediated GaN growth

There has been no changes since our last update on 8/31/14. The award was on a no cost extenion while we were waiting for the result of the renewal (which was not funded).

- We can now grow 50 nm thick films of oxygen-doped GaN at room temperature; this was achieved by increasing the repetition rate of the ultraviolet pulsed laser used for surface plasmon-mediated atomic nitrogen formation from 1 Hz → 20 Hz. These 20 Hz 'high repetition rate' samples are a significant step beyond our work reported in June, where few-monolayer films (characterization reported here) were grown by 1 Hz low repetition rate laser growth.
- Despite oxygen contamination in the GaN film, XPS shows that the low temperature GaN films have a valence state profile for nitrogen similar to that seen in commercial GaN films.
- Oxygen contamination in the GaN films is limited by leaks in the vacuum seals in our present growth chamber (base pressure ~$2x10^{-7}$ Torr); we believe that with some chamber modifications and additional pumping, base pressures in the ~10^{-9} Torr or below pressure range could be achieved, and that this would allow us to overcome the oxygen contamination of the GaN films.

2. Characterization of low-repetition rate growth samples

During our last update in June, we reported the growth of mixed gallium oxide/GaN samples that had a N:O:Ga ratio of 1:8:4. At that time, our results indicated that our surface plasmon mediated GaN deposition process had generated GaN compounds, but the presence of ambient oxygen affected the purity of those samples.

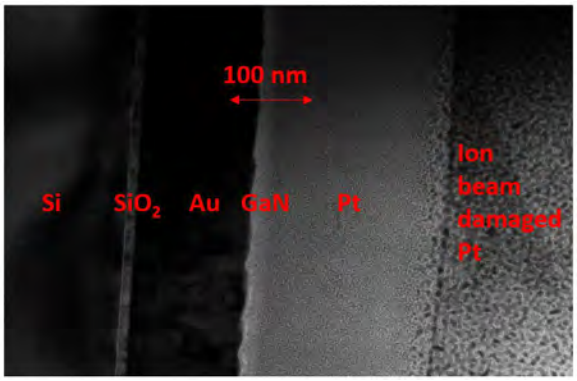

Figure 1: TEM cross section image of GaN/Ga_2O_3 film grown on gold/Si substrate.

Since then, we have worked on TEM imaging of the 1:8:4 GaN samples. Figure 1 shows a TEM image of the GaN sample grown at a low laser repetition rate of 1Hz, which we previously reported to result in a mixed composition of GaN/Ga_2O_3. The TEM sample is prepared by focused ion beam (FIB) milling a cross-section of the GaN film and lifting out the milled cross-section onto a TEM holder. Further FIB was performed to thin the cross section to electron transparency to facilitate TEM observation. The cross section shown here indicates a GaN/Ga_2O_3 layer < 10 nm thick. However, energy dispersive X-ray spectroscopy (EDS) analysis of this layer has shown this layer has a Ga to Pt ratio of 1:1, which indicates that it is difficult to

distinguish the thin GaN film from the Pt film deposited after growth as part of the FIB fabrication procedure. (The Pt deposition is used a capping layer to protect the GaN film surface from Ion beam damage during the FIB process).

3. Growth and characterization of high-repetition rate growth samples

In order to grow thicker GaN films and minimize oxygen contamination, we increased the flux of elemental Ga and atomic N by increasing the Ga effusion cell flux and pulsed laser repetition rate for atomic nitrogen formation from 1 Hz to 20 Hz, respective. optimize the relative flux of elemental Ga and plasmonically dissociated hydrazine in our growth chamber for the formation of higher purity GaN films, by tuning the UV laser repetition rate. The film growth rate varied from 0.2 nm/sec to 0.5 nm/sec. Using this approach we have been able to grow optically transparent GaN samples up to ~50nm thick (thickness characterized by profilometry) at a laser rep rate of 20 Hz. Our GaN film samples are nanocrystalline, as shown in the scanning electron microscope image of Figure 2.

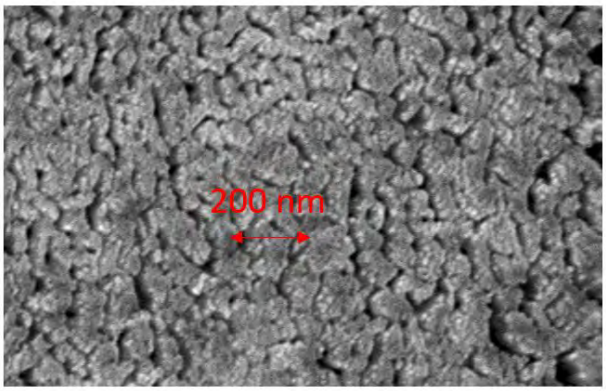

Figure 2: SEM image of surface of GaN film grown on gold substrate at laser repetition rate of 20 Hz.

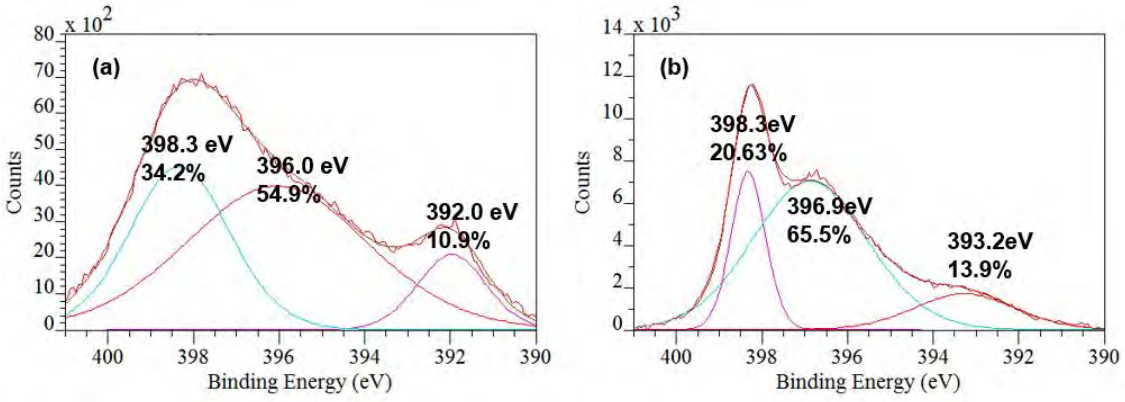

Figure 3: XPS characterization at nitrogen 1s of (a) GaN film grown on gold substrate at 20 Hz (b) commercial GaN crystal on silicon wafer.

Figure 3a shows XPS characterization near the nitrogen 1s binding energy for the GaN film grown on a gold substrate at a laser repetition rate of 20 Hz, in comparison with XPS characterization of a commercial MOCVD-grown GaN film grown on a silicon (001) wafer

(Figure 3b). Our GaN sample and commercial GaN crystal shows similar nitrogen 1s binding energy profiles. The peak fitting indicates that there are three different nitrogen containing chemical bond formation. The peak at 398.3eV, which is at the same energy as nitrogen 1s binding energy in standard data base, is attributed to adsorbed molecular nitrogen on the sample surface. The other two peaks shifted to lower binding energy are due to chemical bond formation of atomic nitrogen with other elements. Compared to the GaN sample previously grown at 1 Hz, which only presented a small shoulder at lower binding energies, the films grown at 20 Hz exhibit a significant improvement in terms of nitride chemical bond formation.

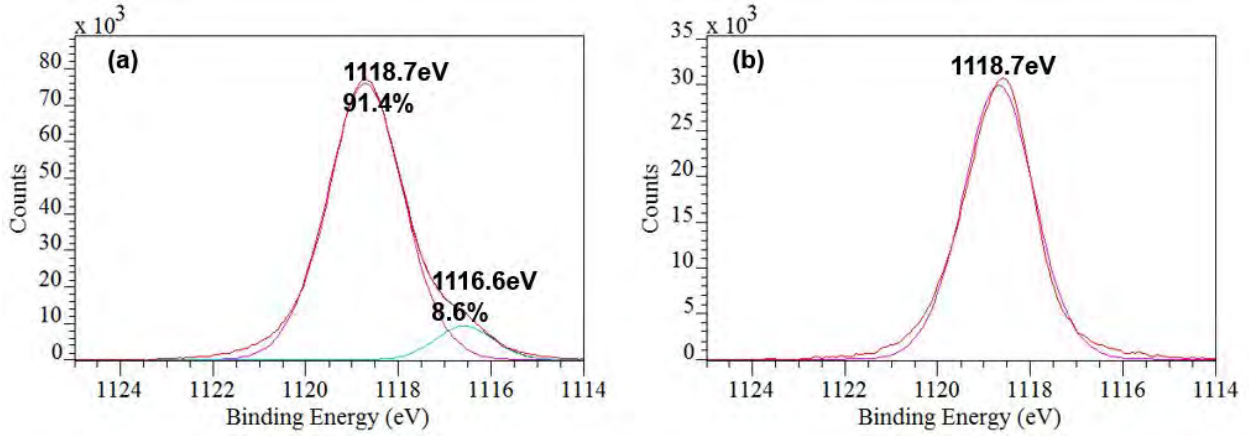

Figure 4: XPS characterization at gallium 2p3/2 of (a) GaN film grown on gold substrate at 20 Hz (b) commercial GaN crystal on silicon wafer.

Figure 4 a and b shows XPS characterization near the Ga $2p^{3/2}$ binding energy. Comparing our GaN sample with commercial GaN crystal, the peak at 1118.7eV is consistent with a valence state change for GaN formation (and possibly also Ga_2O_3 formation). The peak at 1116.6eV indicates that we still have 8.6% Ga present, suggesting that the Ga effusion cell flux was slightly too high to enable full reactive compound synthesis. To be more quantitative about sample oxidation, we also studied oxygen 1s binding energy. From the oxygen 1s peak analysis, we can conclude that the oxygen content is definitely higher in our GaN sample. The peak at 532.7eV is attributed to adsorbed oxygen molecules on the surface. We note that in our nanocrystalline GaN films, there is greater surface area for adsorption of oxygen molecules than on the crystalline GaN film/Si wafers. The peak at 531.5eV in Figure 5a may be attributable to Ga_2O_3 formation, which is not observed the GaN film/Si spectra in Figure 5b.

We note that XPS characterization only probes the elemental composition of the films surface within the <10nm electron escape depth for photoemission. In order to study the film stoichiometry at greater depth, we also performed energy dispersive X-ray spectroscopy (EDS) characterization. Table 1 shows comparison of the relative gallium, nitrogen and oxygen content in our GaN sample compared to commercial GaN wafer. Even though XPS characterization shows close chemical composition profile of our GaN sample and the commercial GaN wafer, EDS characterization indicates that our bulk content has much more oxygen than GaN crystal. The similarity could be attributed to higher-than-ideal growth chamber pressure. Known sources of oxygen contamination include an oxygen leak through the

cold stage used for cryogenic adsorption of hydrazine, so we are unfortunately spuriously cryo-pumping oxygen onto our cold stage, in addition to hydrazine.

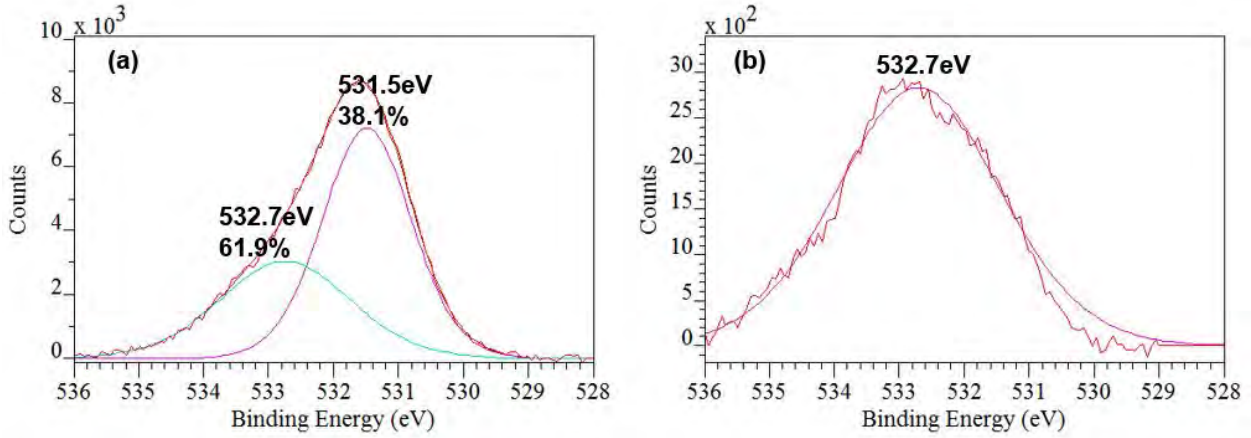

Figure 5: XPS characterization at oxygen 1s of (a) GaN film grown on gold substrate at 20 Hz (b) commercial GaN crystal on silicon wafer.

Atomic %	Gallium	Nitrogen	Oxygen
GaN film sample	29.6	29.9	30.5
Commercial GaN/Si wafer	50.4	41.8	7.8

Table 1: EDS data of the GaN film grown on gold substrate at 20 Hz versus commercial GaN wafer

We can conclude from characterization of the high repetition rate GaN samples that improvement the GaN film stochiometry is facilitated by growth at a higher laser repetition rate, enabling film deposition to compete with ambient contamination. Moving forward, our goal is to achieve a growth chamber pressure than can enable high purity GaN films to be grown by reducing the oxygen content in the bulk of our films. This will require some chamber modifications to seal leaks and will also require additional pumping. Further steps to improve film quality might include in situ surface treatment of the growth substrate prior to film deposition to eliminate adventitious contaminants from the gold-coated substrate surface, so as to better initiate stoichiometric GaN growth rather than Ga_2O_3 growth. Despite the fact that our films still contain oxygen contamination at present, we have been able to demonstrate growth of thick (~ 50 nm) films of oxygen-doped GaN at room-temperature, and thus it appears that the surface plasmon-mediated growth process may be capable of stoichiometric GaN film formation at room temperature if oxygen doping can be eliminated.